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**EDGEWOOD ARSENAL
TECHNICAL REPORT**

EATR 4491

**CONVERSATIONAL COMPUTATION METHOD
FOR FITTING THE ANTOINE EQUATION
TO VAPOR PRESSURE-TEMPERATURE DATA**

by

Elwin C. Penski

Leo J. Latour, Jr., SP4

February 1971



**DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Research Laboratories
Chemical Research Laboratory
Edgewood Arsenal, Maryland 21010**

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EDGEWOOD ARSENAL TECHNICAL REPORT

EATR 4491

CONVERSATIONAL COMPUTATION METHOD FOR FITTING THE ANTOINE
EQUATION TO VAPOR PRESSURE-TEMPERATURE DATA (U)

by

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Physical Chemistry Department

February 1971

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Project 1B062116AD10

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Research Laboratories
Chemical Research Laboratory
Edgewood Arsenal, Maryland 21010

FOREWORD

The work described in this report was authorized under Project 1B062116AD10, Search for Potential Chemical Agents (U). This work was started in March 1969 and completed in October 1970. The data are recorded in notebook 8463.

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DIGEST

A least-squares technique has been developed for determination of the constants of the Antoine equation. The method involves use of the procedure of search by golden section. A conversational FORTRAN program is provided with results of sample runs utilizing data from the open literature. The method gives accurate fits, though the constants calculated differ slightly from the literature constants because the method described is for fitting data that have a relatively constant percentage error rather than a constant absolute error. The former is usually more appropriate when values are measured over a wide range of temperatures. Plots are provided automatically through the use of a teleplotter.

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CONVERSATIONAL COMPUTATION METHOD FOR FITTING THE ANTOINE EQUATION TO VAPOR PRESSURE-TEMPERATURE DATA

I. INTRODUCTION.

The vapor pressure of a pure compound is a unique function of temperature. It is a property required for many calculations in physical chemistry, chemical engineering, and numerous other disciplines. Equations relating to vapor pressure and temperature are required to summarize vapor pressure data; to permit the use of the data in computer programs; and for smoothing, interpolation, extrapolation, and determining heats of vaporization. One of the most widely used equations for fitting vapor pressure-temperature data is the Antoine equation,¹ the use of which has been reviewed by Thomson.²

In addition to fitting vapor pressure data, the Antoine equation may be used to fit densities, fugacities of liquids, kinematic viscosities, relative vapor pressures, and other types of data. The Antoine equation, which has its basis in the well-known Clapeyron equation (see any elementary physical chemistry text), is*

$$\frac{dP}{dT} = \frac{\Delta H_v}{T\Delta V} \quad (1)$$

where

P = vapor pressure

T = absolute temperature

ΔH_v = heat of vaporization

ΔV = change in volume associated with vaporization

If the molar volume of the liquid is negligible compared with that of the vapor and the vapor is a perfect gas, then the Clausius-Clapeyron equation is applicable.

$$\frac{d \ln P}{d(1/T)} = - \frac{\Delta H_v}{R} \quad (2)$$

This equation may be integrated, if ΔH_v is constant, to give

$$\log P = A - B/T \quad (3)$$

where A and B are parameters. The equation also may be written as follows:

$$\log P = A - B/(t + 273.16) \quad (4)$$

where t is temperature in °C.

The Antoine equation results from replacing the value 273.16 in equation (4) with a parameter C .

*All terms are defined in the glossary at the end of the text.

$$\log P = A - B/(t + C) \quad (5)$$

This equation has been found to be adequate, except for data of very high precision, over the range from the triple point to reduced pressures of 0.75.²

The advantages of the Antoine equation include the following: small number of constants required, temperature may be made the dependent variable by a simple inversion, and extrapolations are believed to be more reliable than for other equations.³

The value for C is usually found to be lower than 273.15 and has often been taken arbitrarily as 230.⁴ The latter value has been found to be typical for organic compounds that are liquids at room temperature. Because calculating the best value for C is a time-consuming task without a computer, the value $C = 230$ frequently is found in the literature.

Equations (2) and (5) can be combined to give the heat of vaporization

$$\Delta H_v = 2.3RB \left(\frac{T}{t+C} \right)^2 \quad (6)$$

II. THEORY.

The Antoine equation [equation (5)] may be written in the form of a linear equation

$$Y = A + BX \quad (7)$$

by use of the transformations

$$Y = \log P \quad (8)$$

$$X = -1/(C+t) \quad (9)$$

A set of Y 's and X 's may be fitted by ordinary linear regression analysis,⁵ which results in the following equations:

$$A = \left(\sum_{i=1,n} Y_i - B \sum_{i=1,n} X_i \right) / n \quad (10)$$

$$B = \frac{n \sum_{i=1,n} X_i Y_i - \left(\sum_{i=1,n} X_i \right) \left(\sum_{i=1,n} Y_i \right)}{n \sum_{i=1,n} X_i^2 - \left(\sum_{i=1,n} X_i \right)^2} \quad (11)$$

where Y_i and X_i are the i th value of Y and X , respectively, and n is the number of points being fitted. Given a set of vapor pressures with the corresponding temperatures, any value of C , A , and B may be found.

The method of standard error of estimate involves minimizing the following function,

$$\sum_{i=1,n} [Y_i (\text{experimental}) - Y_i (\text{calculated from eq 6})]^2$$

which will be referred to as S . In this case, S may be considered a function of C alone because both A and B are known functions of C for a given set of experimental data. Because S may not be minimized analytically by any simple known method, values of S are calculated for varying values of C until a minimum value of S is found.

The following equation results from the above discussion:

$$S = \sum_{i=1,n} [Y_i - A - BX_i]^2 \quad (12)$$

Expansion yields

$$S = \sum_{i=1,n} (A^2 + 2ABX_i + B^2X_i^2 + Y_i^2 - 2AY_i - 2BX_iY_i) \quad (13)$$

Summing terms individually gives

$$S = nA^2 + 2AB \sum_{i=1,n} X_i + B^2 \sum_{i=1,n} X_i^2 + \sum_{i=1,n} Y_i^2 - 2A \sum_{i=1,n} Y_i - 2B \sum_{i=1,n} X_i Y_i \quad (14)$$

which is used in the computer program to determine S .

The search method used to find the best value of C involves division of a line segment by a method developed by Euclid. The method, called the search by golden section procedure and described in detail by Wilde,⁶ had great mystical significance among scholars of the Renaissance. This search method was selected because it does not require advance knowledge of how many calculation steps are required. It involves division of a line segment into two unequal parts so that the ratio of the whole to the larger part is equal to the ratio of the larger to the smaller segment.

In mathematical terms this definition leads to the following two equations:

First,

$$L_j = L_{j+1} + L_{j+2}$$

where

$$\begin{array}{l} L_j = \text{length of a line} \\ L_{j+1}, L_{j+2} = \text{length of segments into which the line is divided} \end{array}$$

Second,

$$\frac{L_j}{L_{j+1}} = \frac{L_{j+1}}{L_{j+2}} \equiv Z$$

It may readily be shown from the above equations that Z must be equal to 1.6180340 and that

$$L_{j+1} = \frac{L_j}{Z} = 0.61803399 L_j$$

After m divisions of the line (which is equivalent to dividing the original line, L_o , m times)

$$L_m = \frac{L_o}{Z^m}$$

As an example, after 24 divisions of the line, L_m is equal to 0.00000965 times the length of the original line, L_o .

The standard error of estimate provided by the program is calculated from the following equation:

$$SD = \left[\frac{S}{n-1} \right]^{1/2} \quad (15)$$

It is emphasized that the values for the logarithm of vapor pressure are used for the dependent variable in the least-squares fit; the calculated logarithms of vapor pressures are subtracted from the logarithms of the measured pressures to calculate the standard deviation. Using the data in this manner prevents excessive weighting of larger pressures in the analysis. Generally, the method tends to weight values as a fixed percentage of the measured value. If the absolute error of the measurement is constant, regardless of the magnitude of the values measured, then the method developed in this report probably will not provide the best possible fit to the data.

III. DESCRIPTION OF COMPUTER PROGRAM.

The program is quite self-explanatory; the first question the program asks is how many pairs of temperature-pressure values are to be entered. This is answered by typing the number of data pairs plus a carriage return. Next, the points are entered; as many as 100 points may be used,

but only 70 characters per line may be entered and recorded by the teletype. There must be a carriage return at the end of each line. If the points are to be entered by paper tape, at the end of each line there must be a carriage return, X-off, and rubout.

The computer queries the operator regarding the need for a data table, after which the equation constants are printed along with the calculated standard deviation and an extrapolated boiling point.* This information is followed by a printout of the experimental and calculated vapor pressure values.

An option then is provided for generating a table of vapor pressures, volatilities, and heats of vaporization over a temperature range and in temperature increments selected by the operator. This information is printed after the molecular weight of the compound is provided.

The program automatically loads the experimental and calculated values of vapor pressure into a file named EZ for plotting on a Typagraph Corporation teleplotter.⁷

Generally, when vapor pressures have been measured only over a narrow range of temperatures or the data are not very accurate, it is better to estimate a value for C and then do a standard linear least-squares fit of the data. When C is calculated and found to be greatly different from similar compounds of comparable molecular weight, one should be suspicious of the data. Thomson² has discussed these matters in detail.

Appendix A defines the items used in the computer program, which is given in appendix B.

IV. SAMPLE CALCULATIONS.

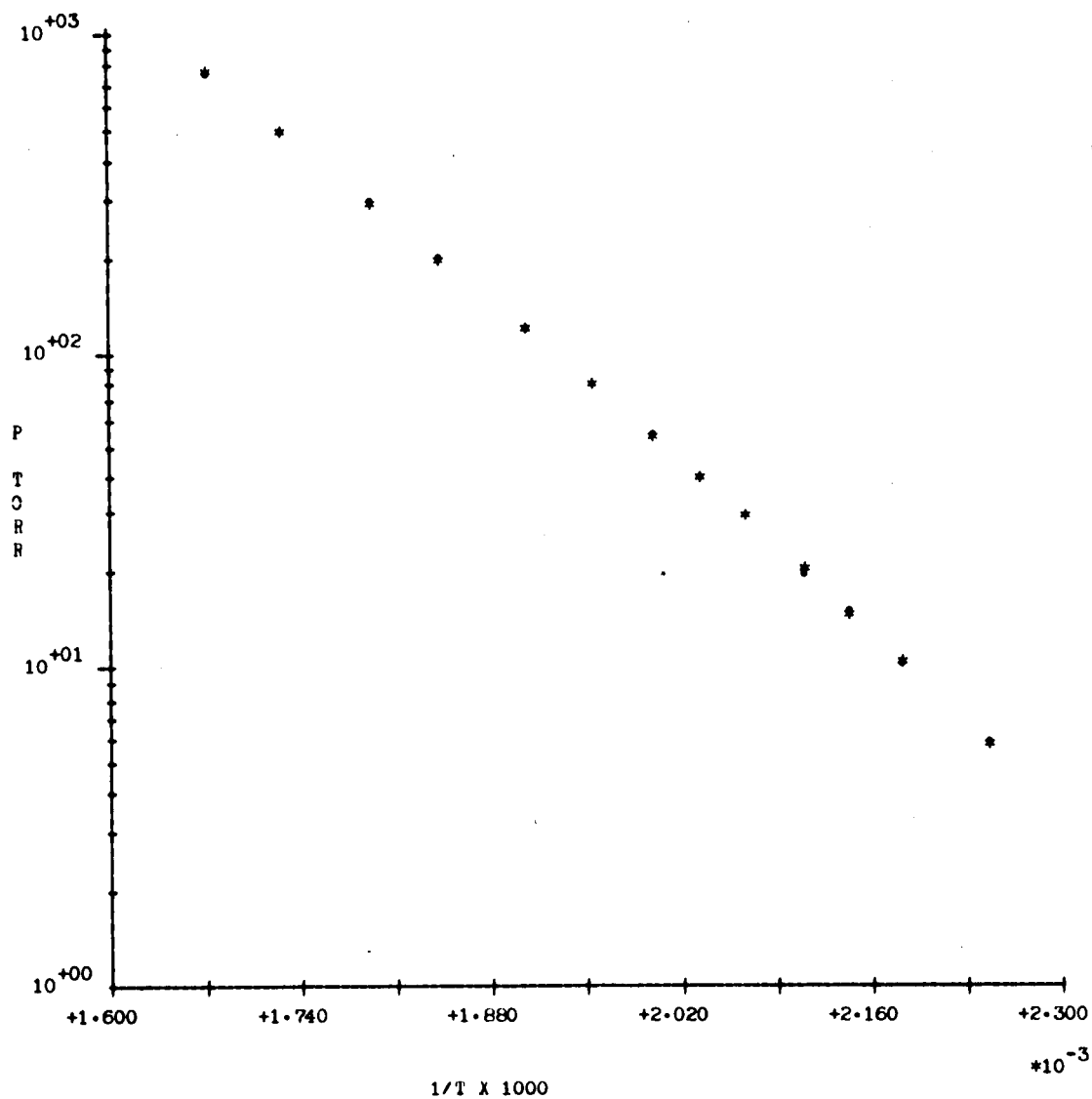
Appendix C provides two sample runs using the reported vapor pressure data of Kremme and Kreps.⁸ The first sample run is for 1-hexadecanol. The vapor pressures for this compound were plotted automatically and are shown in the figure. Although Kremme and Kreps used a different method of determining the Antoine constants, they are in good agreement with the values calculated, as shown in table I. The parameters differ by 1%, and the average and maximum errors of estimate are comparable.

The second sample run is for 1-tetradecanol. This sample run demonstrates a situation in which C is found to be outside the range from 100 to 273.16. In this case, the constants differ significantly from those determined by Kremme and Kreps.⁸

It was found that the Antoine constants of Kremme and Kreps led to different errors of the estimate than were reported. Recalculation of the errors with their data and constants shows a maximum error of 11.4% instead of the reported value of 1.665%. Table II provides the results of the recalculation.

This computer program was run also with the vapor pressure data of isobutyl borate reported by Christopher and Shilman.⁹ The calculated boiling point of 210.4°C agreed exactly with their value. They calculated a heat of vaporization of 12.345 kcal/mole, which compared favorably with the value of 12.33 obtained in this study.

*Caution should be exercised in using extrapolated vapor pressure values. Depending on the change in heat of vaporization with temperature and the extent of extrapolation, significant errors may result.



SYMBOL	NO. PTS.	LEGEND
•	13	-? EXPERIMENTAL
*	13	-? CALCULATED

Figure. Typograph Plot of Vapor Pressure Versus Reciprocal Absolute Temperature for 1-Hexadecanol

Table I. Comparison of Data Fits by Kremme and Kreps* With Sample Runs

Compound	Antoine constants			Error of estimate		Calculation method
	A	B	C	Avg	Max	
1-Hexadecanol	7.04183	1880.126	127.123	1.180	3.569	Kremme & Kreps. This report.
	7.06077	1893.76	128.406	1.189	3.536	
1-Tetradecanol	6.48407	1412.907	95.368	0.793	1.665	Kremme & Kreps. Recalculated. This report.
	6.21962	1244.90	75.600	1.6 2.072	11.4 5.775	

*Kremme, H. R., and Kreps, S. I. J. Chem. Eng. Data 14, 98 (1969).

Table II. Recalculated 1-Tetradecanol Data

Temp	Vapor pressure		Difference
	Exper	Calcd	
°C	Torr		%
151.6	5.2	5.8	11.4
163.0	10.5	10.4	-1.3
171.0	15.3	15.1	-1.1
177.0	19.9	19.8	-0.5
188.4	32.1	32.0	-0.4
199.1	48.4	48.5	0.2
213.3	80.1	80.7	0.7
225.7	120.0	121.2	1.0
243.1	202.8	204.0	0.6
257.8	302.6	304.4	0.6
277.9	501.2	499.8	-0.3
295.9	755.2	746.4	-1.2

The program, with slight modification, may be used to fit other physicochemical data; i.e., densities, fugacities of liquids, kinematic viscosities, etc.

V. CONCLUSIONS.

A conversational FORTRAN computer program is described that calculates the constants required for solution of the Antoine equation for vapor pressure-temperature data. Convenient printouts of experimental data used, calculated vapor pressure data, volatility data, heats of vaporization, and an estimated normal boiling point are provided. In addition, the standard error of estimate is calculated.

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GLOSSARY

A, B, C	Parameters of the Antoine equation
ΔH_v	Heat of vaporization
L_j	Line segments where j is number of divisions by golden section method
n	Number of data points
P	Vapor pressure
R	Ideal gas law constant
S	Sum of the squares of differences between calculated and measured values of $\log P$
SD	Standard error of estimate
t	Temperature in $^{\circ}\text{C}$
T	Temperature in $^{\circ}\text{K}$
ΔV	Change in volume associated with vaporization
X	Reciprocal of $-(C + t)$
X_i	The i th value of X
Y	Logarithm of P
Y_i	The i th value of Y
Z	Ratio of successive lengths by golden section

APPENDIXES

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APPENDIX A

DEFINITIONS OF TERMS IN PROGRAM

A, B	Parameters in the Antoine equation
BP	Boiling point calculated from Antoine equation
B9	Maximum allowable range of uncertainty associated with the value of parameter C
C	Parameter in the Antoine equation
C1	Log P calculated from Antoine equation
C2	P calculated from Antoine equation
D1	Controls printing of optional data table
G	Linear array of measured pressure values
GOLD	Line segment from golden section method
H	Maximum temperature used in optional output table
I	subscript
IC	Subscript to be used in sub-routine names COMP to select C
INT	Interval of temperature for calculating table
I1, J, K, K1	Subscripts
L	Subscript or lowest temperature in optional output table
L1	Subscript
N1	Number of data points
N9	Controls printing of diagnostic message
PCD	Percent difference between measured and calculated pressures
PRC	Pressure calculated from Antoine equation
RDT	Reciprocal of temperature in °K
SD	Standard error of estimate
S1	Sum of X_i 's

S2	Sum of X_i^2 's
S3	Sum of $(X_i * Y_i)$'s
S4	Sum of Y_i 's
S5	Sum of Y_i^2 's
T	Linear array of experimental temperatures in °C
T1	Temperature used for calculating optional output table
V	Linear array of successive values of S
W	Linear array of trial values of parameter C
W1	Lowest value of C used; normally 100
W2	Highest value of C used; normally 273
X	Reciprocal of $-(C + t)$
Y	Linear array of common logarithms of measured pressure values

APPENDIX B

PROGRAM LISTING

The language used is CALL/360: FORTRAN**. CALL/360 is a system designed to provide the enormous efficiency of fast turnaround conversational computing with immediate access to the full capabilities of a large computer, IBM 360/65 in this case, at a conveniently located remote terminal. Because a few of the features of this subset of FORTRAN may not be familiar to some readers, they are discussed below.

First, the REAL*8 specification statement establishes variables as real constants of eight locations or approximately 16.8 decimal digits of precision. The rest of the real floating point variables are about 7.2 decimal digits. Second, the percentage symbol at the end of a line replaces the continuation number commonly used with cards. Third, the "*" used in the READ commands in place of a format statement number indicates that the format to be used for data input is list directed. In this format, data items are separated by either a comma or a blank space.

**CALL/360 FORTRAN Language Reference Manual. G320-1054-0. International Business Machines Corporation, New York, New York. 1970.

```

100 "TITLE: ANTOINE
105 "PROGRAM TO FIND CONSTANTS FOR THE ANTOINE EQUATION
110     COMMON Y(100), T(100), S4, S5, A, B, W(4), V(4), N1, IC
115     DIMENSION G(100)
120     REAL*8 Y, T, S4, S5, A, B, AFL
125     CALL OPEN(1, 'EZ', 'OUTPUT')
130 "INPUT SECTION
135     WRITE(6,100)
140 100 FORMAT(/' UNITS:  TEMPERATURE      CENTIGRADE'/'
145     '                PRESSURE        TORR'/)
150 1  WRITE(6,10)
155 10 FORMAT('  HOW MANY POINTS?')
160     READ(5,*)N1
165     S4=0
170     XXX=1E37
175     XXL=9E37
180     S5=0
185     WRITE(6,11)
190 11 FORMAT(' DATA:  T1,P1,T2,P2,.....')
195     READ(5,*)(T(I),G(I),I=1,N1)
200 "CALCULATE LOGS OF VAPOR PRESSURES, SUM OF LOGS, AND SUM
205 "OF LOGS SQUARED
210     DO 20  I=1, N1
215     RTK=1.0/(273.16+T(I))
220     WRITE(1) RTK,G(I)
225     Y(I)=ALOG10(G(I))
230     S4=S4+Y(I)
235     S5=S5+Y(I)*Y(I)
240 20  CONTINUE
245     WRITE(1) XXX,XXX
250 140 WRITE(6,12)
255 12 FORMAT('  DATA TABLE? (1=YES; 0=NO)')
260     READ(5,*) D1
265 41 FORMAT(9X'TEMPERATURE'6X'PRESSURE'/)
270     IF( D1 .LT. 0.5 ) GO TO 156
275     WRITE(6,41)
280     DO 40  I=1, N1
285     WRITE(6,87) T(I),G(I)
290 87  FORMAT(3X,1PE16.4,1PE16.3)
295 40  CONTINUE
300 "DEFINE RANGE OF SEARCH
305 156 W1=100
310     W2=273.15
315 " BEGIN SEARCH
320 160 CONTINUE
325 "SET LIMIT OF UNCERTAINTY (B9) ALLOWABLE FOR C

```

```

330      E9=0.005
335      I=1
340      J=2
345      K=3
350      L=4
355  "THE FOUR POINTS INVOLVED IN THE SEARCH ARE STORED IN
360  "      W(N), N=1,4 IN AN ORDER DETERMINED BY PROGRESS
365  "      OF SEARCH
370      W(I)=W1
375      IC=I
380      CALL      COMP
385      W(L)=W2
390      IC=L
395      CALL      COMP
400 184 GOLD=W(L)-W(I)
405      GOLD=GOLD*.61803399
410      IF(GOLD.LT.E9) GO TO 258
415      W(K)=W(I)+GOLD
420      IC=K
425      CALL      COMP
430  "IF STATEMENTS INVOLVING V(N) DETERMINE WHICH LINE SEGMENTS
435  "TO
440      IF( V(I).GT.V(L)) GO TO 202
445      L=1
450      I=4
455 202 IF( V(K).LT.V(L)) GO TO 214
460      L=4
465      W(I)=W(K)
470      V(I)=V(K)
475      I=1
480      GO TO 184
485 214 L=4
490      I=1
495 218 GOLD=GOLD*.61803399
500      IF( GOLD.LT.E9) GO TO 258
505      W(J)=W(I)+GOLD
510      IC=J
515 226 CALL      COMP
520      IF( V(J).LT.V(K)) GO TO 248
525      I=I
530      I=J
535      J=K
540      K=I1
545      IF( GOLD.LT.E9) GO TO 258
550      W(K)=W(I)+GOLD
555      GOLD=GOLD*.61803399
560      IC=K
565      GO TO 226

```

```

570 248 L1=L
575     L=K
580     K=J
585     J=L1
590     GO TO 218
595 "DETERMINE WHETHER C IS IN THE INITIAL RANGE
600 258 IF(W1.EQ.W2) GO TO 301
605     IC=J
610     IF( W(1).GT.W1) GO TO 266
615     IC=I
620     GO TO 356
625 266 IF( W(L).LT.W2) GO TO 300
630     IC=L
635     GO TO 362
640 301 IC=I
645 300 CONTINUE
650     C=W(IC)
655     WRITE(6,29)
660 29  FORMAT('O LOG P=A-B/(C+T)')
665     WRITE(6,28) A,E,W(IC)
670 28  FORMAT('O  A'5X,1PE12.5/3X'B'5X,1PE12.5/3X'C'5X,1PE12.5)
675     SD=SQR1(V(IC)/(N1-1))
680     WRITE(6,27) SD
685 27  FORMAT('O STANDARD DEVIATION'3X,1PE12.5)
690     BP=-B/(2.88081-A)-C
695     WRITE(6,26)BP
700 26  FORMAT('O BOILING POINT      ' 4X,1PE12.5)
705     WRITE(6,38)
710 38  FORMAT('O TEMPERATURE'21X'PRESSURE'18X'PERCENT'/'X
715     22X'EXPERIMENTAL'5X'CALCULATED'10X'DIFFERENCE' )
720     DO 111 I=1,N1
725     PRC=A-B/(C+T(I))
730     PRC=10.**PRC
735     PCD=(PRC-G(I))*100.0/G(I)
740 43  FORMAT(2X,F8.3,12X,F11.5,5X,F11.5,6X,F11.5)
745     RTK=1.0/(273.16+T(I))
750     WRITE(1) RTK,PRC
755 111 WRITE(6,43) T(I), G(I), PRC, PCD
760     WRITE(1) XXL,XXL
765     CALL CLOSE(1)
770 39  FORMAT('O TABLE? GIVE: LOWEST,HIGHEST AND INCREMENT OF X
775     TEMPERATURE'/' AS INTEGERS (0,0,0 MEANS NO)')
780     WRITE(6,39)
785     READ(5,*) L,H,INT
790     IF( L.EQ.H) GO TO 387
795     WRITE(6,101)
800 101 FORMAT('/' GIVE MOLECULAR WEIGHT')
805     READ(5,*) XMOL

```

```

810      WRITE(6,46)
815 46  FORMAT(' TEMPERATURE      VAPOR PRESSURE      VOLATILITY%
820      HEAT OF VAPORIZATION')
825      T1=L
830      R=0.082053
835      CON=1.9872E-3*2.3026
840 344 C1=A-B/(C+11)
845 346 IF(T1.GT.H) GO 10 388
850      C2=10.0**C1
855      TK=T1+273.15
860      VOL=C2*XMOL/(R*TK*760.0)*1.0E+06
865      HEAT=CON*R*(TK/(11+C))**2
870      WRITE(6,59) T1, C2, VOL,HEAT
875 59  FORMAT(2X, F10.3, F16.5, F16.3, F16.3)
880      T1=T1+IN1
885      GO 10 344
890 356 WRITE(6,49) W(IC)
895 49  FORMAT('O C LESS THAN '1FE12.5)
900      GO 10 366
905 362 WRITE(6,48) W(IC)
910 48  FORMAT('O C GREATER THAN '1FE12.5)
915 366 IF(N9.GT.0) GO 10 378
920      N9=3
925      WRITE(6,47)
930 47  FORMAT('OTHE CONSTANT C IN LOG P=A+B/(C+1) IS ESTIMATED TO BE'//%
935      ' OUTSIDE THE RANGE 100 TO 273. TO CONTINUE, SPECIFY THE'//%
940      ' ENDPOINTS OF ANOTHER RANGE. IF BOTH ENDPOINTS ARE THE'//%
945      ' SAME, THE CALCULATION WILL BE DONE USING THAT VALUE FOR'//%
950      ' C. 0.0 WILL STOP THE ANALYSIS.')
955 378 CONTINUE
960      READ(5,*) W1,W2
965      IF(W1.EQ.0) GO 10 387
970      GO 10 160
975 388 WRITE(6,390)
980 390 FORMAT(/' UNITS: VOLATILITY      MILLIGRAMS/CUBIC METER'//%
985      ' HEAT OF VAPORIZATION      KCAL/MOLE'//)
990 387 WRITE(6,389)
995 389 FORMAT (' MORE DATA? ( 1=YES, 0=NO )')
1000      READ(5,*)D1
1005      IF (D1 .LT. 0.5) GO 10 999
1010      WRITE (6,391)
1015 391 FORMAT(' NEW FILE NAME ')
1020      READ (5,*) AFL
1025      CALL OPEN (1,AFL,'OUTPUT')
1030      GO TO 1
1035 999 END

```



```

1050      SUBROUTINE      COMP
1055      COMMON Y(100), T(100), S4, S5, A, B, W(4), V(4), N1, IC
1060      REAL*8 Y, T, S1, S2, S3, S4, S5, A, B, X
1065      S1=0
1070      S2=0
1075      S3=0
1080      DO 50 K1=1, N1
1085      X=-1.0/(T(K1)+W(IC))
1090      S1=S1+X
1095      S2=S2+X*X
1100      S3=S3+Y(K1)*X
1105 50    CONTINUE
1110      B=(N1*S3-S1*S4)/(N1*S2-S1*S1)
1115      A=(S4-B*S1)/N1
1120      V(IC)=N1*A**2+2.0*A*B*S1+B*B*S2+S5-2.0*A*S4-2.0*B*S3
1125      RETURN
1130      END

```

APPENDIX C

SAMPLE RUNS

RUN

ANTOINE 11:34 10/27/70 TUESDAY LEA

UNITS: TEMPERATURE CENTIGRADE
PRESSURE TORR

HOW MANY POINTS?

? 13

DATA: T1,P1,T2,P2,.....

? 172.1,5.9, 185.3,10.3, 193.4,15.1, 201.0,19.8? 211.0,30.1, 218.6,40.4, 227.3,55.3, 238.7,80.3? 251.6,120.3, 269.3,200.5, 285.0,302.1, 305.9,502.4, 325.1,759.2

DATA TABLE? (1=YES; 0=NO)

? 1

TEMPERATURE	PRESSURE
1.7210D+02	5.900E+00
1.8530D+02	1.030E+01
1.9340D+02	1.510E+01
2.0100D+02	1.980E+01
2.1100D+02	3.010E+01
2.1860D+02	4.040E+01
2.2730D+02	5.530E+01
2.3870D+02	8.030E+01
2.5160D+02	1.203E+02
2.6930D+02	2.005E+02
2.8500D+02	3.021E+02
3.0590D+02	5.024E+02
3.2510D+02	7.592E+02

LOG P=A-E/(C+1)

A 7.06077D+00
E 1.89376D+03
C 1.28406E+02

STANDARD DEVIATION 7.08865E-03

BOILING POINT 3.24650E+02

TEMPERATURE	PRESSURE		PERCENT DIFFERENCE
	EXPERIMENTAL	CALCULATED	
172.100	5.90000	5.73942	-2.72167
185.300	10.30000	10.56907	2.61235
193.400	15.10000	14.99629	-0.68683
201.000	19.80000	20.50014	3.53603
211.000	30.10001	30.27901	0.59469
218.600	40.39999	40.11848	-0.69681
227.300	55.30000	54.55376	-1.34945
238.700	80.30000	79.82768	-0.58819
251.600	120.30000	119.47359	-0.68696
269.300	200.50000	199.09674	-0.69988
285.000	302.10010	301.92554	-0.05778
305.900	502.39990	501.58472	-0.16226
325.100	759.19995	767.27490	1.06361

TABLE? GIVE: LOWEST, HIGHEST AND INCREMENT OF TEMPERATURE
AS INTEGERS (0,0,0 MEANS NO)

? 150, 350, 10

GIVE MOLECULAR WEIGHT

? 242.45

TEMPERATURE	VAPOR PRESSURE	VOLATILITY	HEAT OF VAPORIZATION
150.000	1.81390	0.17E+05	20.018
160.000	3.12226	0.28E+05	19.546
170.000	5.18220	0.45E+05	19.110
180.000	8.32321	0.71E+05	18.708
190.000	12.97603	0.11E+06	18.334
200.000	19.69006	0.16E+06	17.987
210.000	29.15074	0.23E+06	17.663
220.000	42.19601	0.33E+06	17.361
230.000	59.83130	0.46E+06	17.078
240.000	83.24406	0.63E+06	16.812
250.000	113.81445	0.85E+06	16.562
260.000	153.12517	0.11E+07	16.327
270.000	202.96800	0.15E+07	16.105
280.000	265.34741	0.19E+07	15.896
290.000	342.48364	0.24E+07	15.698
300.000	436.80786	0.30E+07	15.510
310.000	550.96069	0.37E+07	15.332
320.000	687.78735	0.45E+07	15.163
330.000	850.32446	0.55E+07	15.002
340.000	1041.79248	0.66E+07	14.848
350.000	1265.58472	0.79E+07	14.702

UNITS: VOLATILITY MILLIGRAMS/CUBIC METER
HEAT OF VAPORIZATION KCAL/MOLE

MORE DATA? (1=YES, 0=NO)

? 0

STOP

UNITS: TEMPERATURE CENTIGRADE
 PRESSURE TORR

HOW MANY POINTS?

? 12

DATA: T1, P1, T2, P2,

? 151.6, 5.2, 163.0, 10.5, 171.0, 15.3, 177.0, 19.9, 188.4, 32.1

? 199.1, 48.4, 213.3, 80.1, 225.7, 120.0, 243.1, 202.8

? 257.8, 302.6, 277.9, 501.2, 295.9, 755.2

DATA TABLE? (1=YES; 0=NO)

? 0

C LESS THAN 1.00000E+02

THE CONSTANT C IN $\log P = A + E/(C + T)$ IS ESTIMATED TO BE OUTSIDE THE RANGE 100 TO 273. TO CONTINUE, SPECIFY THE ENDPOINTS OF ANOTHER RANGE. IF BOTH ENDPOINTS ARE THE SAME, THE CALCULATION WILL BE DONE USING THAT VALUE FOR C. 0.0 WILL STOP THE ANALYSIS.

? 50, 100

$\log P = A + E/(C + T)$

A 6.21961E+00

E 1.24490E+03

C 7.55994E+01

STANDARD DEVIATION 1.16157E-02

BOILING POINT 2.97258E+02

TEMPERATURE	PRESSURE		PERCENT DIFFERENCE
	EXPERIMENTAL	CALCULATED	
151.600	5.20000	5.49919	5.75361
163.000	10.50000	10.04831	-4.30181
171.000	15.30000	14.83733	-3.02398
177.000	19.89999	19.55545	-1.73137
188.400	32.10001	31.92149	-0.55611
199.100	48.39999	48.72598	0.67353
213.300	80.10001	81.37863	1.59629
225.700	120.00000	122.41991	2.01659
243.100	202.80000	205.79420	1.47643
257.800	302.60010	305.95801	1.10968
277.900	501.19995	498.85498	-0.46787
295.900	755.19995	738.93457	-2.15378

TABLE? GIVE: LOWEST, HIGHEST AND INCREMENT OF TEMPERATURE AS INTEGERS (0.0, 0.0 MEANS NO)

? 0, 0, 0

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13. ABSTRACT A least-squares technique and a search method are combined for determination of the constants of the Antoine equation for vapor pressure data. The method is designed for fitting data that have a relatively constant percentage error rather than a constant absolute error. A conversational FORTRAN program is provided with results of sample runs utilizing data from the open literature. The calculation also provides estimates of heats of vaporization and normal boiling point. Plots of the data are provided automatically through the use of a teleplotter.		
14. KEYWORDS Vapor pressure Antoine equation Conversational computation Least squares Boiling point Heat of vaporization Computer program Volatility Physical chemistry Plotting		

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